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(54) **COMPOSITION OF EPOXY RESIN AND EPOXY-REACTIVE POLYPHOSPHONATE**

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This patent is subject to a terminal disclaimer.

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**C08L 63/02** (2006.01)

(52) **U.S. Cl.** ..... **525/523**; 528/219; 528/398

(58) **Field of Classification Search** ..... None  
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,617,584 A \* 10/1986 Ikeya et al. .... 257/793  
7,427,652 B2 \* 9/2008 Levchik et al. .... 525/486  
7,449,526 B2 \* 11/2008 Levchik et al. .... 525/523

FOREIGN PATENT DOCUMENTS

JP 2001-19746 A \* 1/2001  
WO 03/029258 4/2003  
WO 2004/044054 5/2004  
WO 2004/060957 7/2004

OTHER PUBLICATIONS

Patent Abstracts of Japan vol. 2000, No. 16, May 8, 2001 & JP 2001-019746, Jan. 23, 2001.

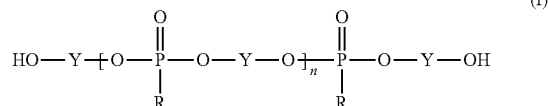
\* cited by examiner

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(57) **ABSTRACT**

An epoxy resin composition comprising an epoxy resin and, as the effective curing agent, an epoxy-reactive polyphosphonate which can be of the formula (I) where "Y" is an arylene and "n" can range from about 2 to about 30.



**16 Claims, No Drawings**

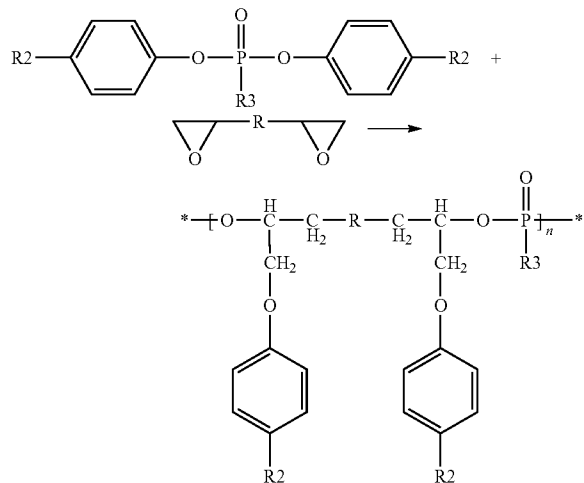
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## COMPOSITION OF EPOXY RESIN AND EPOXY-REACTIVE POLYPHOSPHONATE

### BACKGROUND OF THE INVENTION

This invention relates to a new use for the type of polyphosphonate material that is described and claimed in U.S. Pat. Nos. 4,331,614 and 4,719,279, which are each incorporated herein by reference. While U.S. Pat. No. 4,035,442 has described polyester filaments having improved flame retardancy due to use of a poly(m-phenylene cyclohexylphosphonate), the instant invention relates to flame retarded epoxy compositions, as will be described in greater detail below. The term "polyphosphonate" as used herein is to be construed as covering oligomeric phosphonate materials as well as those of higher molecular weight.

Shouji Minegishi describes the reaction of epoxy compounds with phosphonates in Journal of Polymer Science, Part A, Polymer Chemistry, Vol. 37, 959-965:



His goal was to prepare polymeric linear phosphonates with little or no residual epoxy. Such polymers can be used as additive type flame retardants.

The present invention relates to an epoxy resin composition that can be used, for example, in printed wiring boards for electronic applications. It represents a new embodiment, for example, over the type of flame retarded epoxy resin compositions described in PCT Patent Publication No. WO 03/029258 where an epoxy resin, which contained the type of polyphosphonate flame retardant additive that is also used in the epoxy resin compositions of the present invention, was cured in the presence of a methylimidazole curing catalyst.

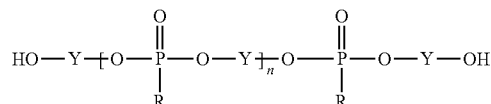
### SUMMARY OF THE INVENTION

The composition of the present invention contains, as one essential component, an epoxy resin. This component is present at from about 50% to about 95%, by weight of the total weight of the composition. This component can be a non-halogen containing epoxy resin, such as a bisphenol A-type of epoxy resin, or other resins of this general type that have utility for the manufacture of printed wiring boards or other electronic substrate materials of that type (for example, bisphenol F epoxy, phenolic novolak epoxy, cresol novolak epoxy, and/or bisphenol A novolak epoxy resins). Compatible mixtures of any of these resins may be employed, if desired.

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The polyphosphonate flame retardant curing agent that forms another essential additive of the compositions of the present invention is generally present at from about 5% to about 50%, by weight of the total weight of the composition, for example, from about 10% to about 35%, by weight. In regard to epoxy compositions of the present invention, and unlike the invention described in PCT Patent Publication No. WO 03/029258, this polyphosphonate functions as the effective curing agent for the epoxy resin.

This curing agent is an polyphosphonate composition having the formula:



where "Y" is an arylene and "n" can range from about 2 to about 30 and R is a lower alkyl. If desired, mixed arylenes and mixed alleylphosphonates can be used to prepare mixed products. This oligomeric or polymeric material has a phosphorus content of greater than about 10%, by weight. The polyphosphonate species in the composition comprise oligomers or polymers of this type that can either contain —OK end groups or not contain such end groups. The individual polyphosphonate species that contain —OH end groups can be monohydroxy or dihydroxy-substituted. The concentration of polyphosphonate species in the composition that contain hydroxy end groups can range from about 20% to about 100%, based upon the total number of termination ends ("chain ends") that potentially could hold such end groups, for example, from about 50% to about 100%. The number of OH terminal groups can be controlled by the ratio of arylene to phosphonate or by using end-capping agents such as triaryl-phosphates. In the former case, if excess arylene-containing diol is used with the phosphonate reagent, for example, in making the polyphosphonate, there will be a higher hydroxyl content in the final product, and vice versa. The preferred R group is methyl, but can be lower alkyl.

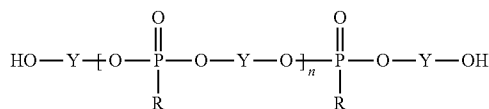
By "Arylene" is meant any radical of a dihydric phenol. The dihydric phenol can have its two hydroxy groups in non-adjacent positions. Examples include the resorcinols; hydroquinones; and bisphenols, such as bisphenol A, bisphenol F, and 4,4'-biphenol, phenolphthalein, 4,4'-thiodiphenol, or 4,4'-sulfonyldiphenol. A small amount of polyhydric phenol, such as a novolac or phloroglucinol, with three or more hydroxyl groups therein can be included to increase the molecular weight. The Arylene group can be 1,3-phenylene, 1,4-phenylene, or a bisphenol diradical unit, but it is preferably 1,3-phenylene.

### DESCRIPTION OF THE PREFERRED EMBODIMENTS

The polyphosphonate curing agent for the epoxy resin composition of this invention can be made by any of several routes: (1) the reaction of an  $\text{RPOCl}_2$  with  $\text{HO-Aryl-OH}$  or a salt thereof, where R is lower alkyl, preferably methyl; (2) the reaction of diphenyl alkylphosphonate, preferably methylphosphonate, with  $\text{HO-Arylene-OH}$  under transesterification conditions; (3) the reaction of an oligomeric phosphite with repeating units of the structure  $-\text{OP}(\text{OR}')-\text{O-Arylene}-$  with an Arbuzov rearrangement catalyst, where R' is lower alkyl, preferably methyl; or (4) the reaction of an oligomeric phosphite with the repeating units having the struc-



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wherein "Y" is an arylene, "n" ranges from about 2 to about 30 and R is a lower alkyl.

2. A composition as claimed in claim 1 wherein the epoxy resin comprises from about 50% to about 95%, by weight of the total weight of the composition.

3. A composition as claimed in claim 1 wherein the epoxy resin comprises from 65% to 90% by weight of the total weight.

4. A composition as claimed in claim 1 wherein the polyphosphonate comprises from about 5% to 50%, by weight of the total weight of the composition.

5. A composition as claimed in claim 1 wherein the polyphosphonate comprises from 10% to 35% by weight of the total weight.

6. The composition of claim 1 wherein the R is methyl and the arylene is 1,3,-phenylene.

7. The composition of claim 1 wherein the epoxy resin is a bisphenol A di-epoxy resin.

8. The composition of claim 1 further comprising a fiber and/or cloth reinforcing agent.

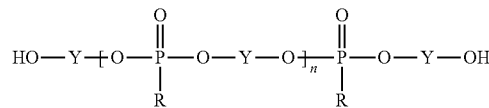
9. The composition of claim 1 further comprising a colorant.

10. The composition of claim 1 further comprising a release agent.

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11. An epoxy resin composition consisting essentially of an epoxy resin, and, as the curing agent, an epoxy-reactive polyphosphonate having formula (1)

(I)  
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(I)

wherein "Y" is an arylene, "n" ranges from about 2 to about 30 and R is a lower alkyl.

12. A composition as claimed in claim 11 wherein the epoxy resin consists essentially of about 50% to about 95%, by weight, of the total weight of the composition.

13. A composition as claimed in claim 11 wherein the epoxy resin consists essentially of 65% to 90% by weight of the total weight.

14. A composition as claimed in claim 11 wherein the polyphosphonate consists essentially of about 5% to about 50%, by weight, of the total weight of the composition.

15. A composition as claimed in claim 11 wherein the polyphosphonate from 10% to 35% by weight of the total weight.

16. The composition of claim 11 wherein the R is methyl and the arylene is 1,3,-phenylene.

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